# POSTER

## LOCAL ORDER AND STRUCTURAL PROPERTIES OF CARBON-BORON-NITROGEN SOLID SOLUTIONS

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## PREPARATION, COMPOSITION, X-RAY STUDIES

A gaseous mixture of boron trichloride, ammonia, and acetylene, diluted in hydrogen, was circulated through a hot-wall reactor at temperatures in the range 1000-1150°C, under a pressure of 10-60 millibars. The deposits are smooth glossy films, up to 100 μm thick. Their composition, which depends upon the conditions of preparation was determined with an electron microprobe, and the results agree very well with the previous findings [1-3]. All the compositions fall inside the triangle bounded by pure carbon, BN, and $BC_3$. X-ray diffraction powder diagrams show that all the films have a hexagonal graphitic turbostratic structure. The carbon-rich CBN and $BC_3$ samples have a much better organization than the carbon-poor CBN or even than a pyrocarbon. The $d_{002}$ values are 0.34 nm for the carbon rich-samples, and 0.35 nm for the carbon-poor one. The $L_c$ dimensions (coherence length along the c-axis) are 12-13 nm for carbon-rich CBN and $BC_3$, 3 nm for the pyrocarbon, and 2 nm for the carbon-poor sample. The higher the carbon content, the better the three dimensional ordering of the graphitic lattice. But the presence of boron obviously also improves the size of the ordered domains.

### "GRAPHITIZATION"

We heat-treated CBN films in a graphite resistor furnace under an argon atmosphere (1 bar). The variations of the interlayer distance $d_{002}$ and the corresponding increase of the coherence length $L_c$ show an obvious "graphitization" effect. A loss of mass could be simultaneously expected, as foreign atoms are driven out of the carbon lattice, but no such effect is observed below 2250°C.
Above 1750°C and below 2500°C there is also some X-ray evidence of the formation of boron carbide ($B_4C$ or $B_{13}C_2$). Finally, above 2500°C there are clearly in the material two phases mixed at the micrometer or nanometer levels, one of them being boron saturated graphite, while the other could be boron nitride.

## RAMAN STUDY

The Raman spectra of our films were obtained in the vicinity of 1500 cm$^{-1}$ with a microprobe consisting of a multicanal Dilor spectrometer coupled with a microscope. All the spectra of as-deposited films show strong wide bands near 1580 cm$^{-1}$ and 1350 cm$^{-1}$, close to the graphite or boron nitride frequencies. Five spectra can be compared on Figure 1: the spectrum of a pure pyrocarbon, and that of a $BC_3$ sample as well as the spectra of three CBN samples with decreasing carbon contents (77, 63, and 22%). The bands overlap (except in the case of pure carbon), the intensity of the 1350 cm$^{-1}$ band is rather strong and could be interpreted as evidence of small crystallite sizes $L_a$. But we must take into account the effect of substituted boron on the Raman spectra of carbon materials, which was investigated by Hagio and coworkers [4], who observed, with increasing boron doping, a widening of the 1580 band and an impressive growth of the intensity of the 1350 cm$^{-1}$ band. We may conclude that the relative intensity of the 1350 cm$^{-1}$ component and the overlapping of the bands in the $BC_3$ and CBN spectra is no indication of a poor crystallinity but an indication of the large amount of boron substituted to carbon in the lattice. In other words, it confirms that these materials are actual solid solutions. The spectra of heat-treated materials show an obvious improvement of the crystal structure as the heat-treatment temperature increases: the relative intensity of the 1350 cm$^{-1}$ band decreases steadily, and so do the widths of the two bands, so that they eventually no longer overlap, and the 1620 cm$^{-1}$ frequency can also be observed as a side line of the $E_{2g2}$ band. All the effects of the boron substitution in the graphitic lattice thus vanish.

## BORON NUCLEAR MAGNETIC RESONANCE

The $^{11}B$ isotope has a natural abundance of 80%, which makes it an easy target to NMR solid state studies. Three as-deposited samples were investigated by NMR. Sample (a) was a carbon-rich film of composition $C_{0.78}B_{0.22}$ corresponding to the approximate formula $BC_3$.

Samples (b) and (c) were ternary compounds of compositions $C_{0.71}B_{0.22}N_{0.07}$ and $C_{0.24}B_{0.39}N_{0.37}$ respectively. All three materials show a wide slightly asymmetrical resonance line, with a small chemical shift. The signal presented in figure 2 is a computer simulation of the observed NMR line of $BC_3$ as an unresolved unsymmetrical doublet (G and D): the two components have the same area, i.e. the same total intensity. They are separated by 10.5 kHz. Such a splitting of the Larmor frequency may be due to the local magnetic field $H_{loc}$ created by another B first-neighbor nucleus. Can there be B pairs at the right distance to generate that coupling ? Three theoretical models of $BC_3$ have been published [5,6]: only one of them involves pairs of boron atoms. From this structure a B-B distance of 0.142 to 0.155 nm can be estimated, and with that distance a splitting of the resonance line of approximately 7.4 to 9.7 kHz is calculated: this is not too different from the observed value of 10.5 kHz. The same interpretation can be proposed for the NMR signal of the ternary compound (b), which is very similar to the $BC_3$ signal, although at a slightly lower frequency. However the simulation of the signal of the carbon-poor compound (c) by a doublet is not satisfactory. A triplet is necessary. This triplet is actually a nearly symmetrical doublet GD with a splitting identical to that of the carbon-rich compounds, plus a singlet D' located at a frequency slightly higher than the D frequency. That single line D' would characterize boron atoms bound to non-boron neighbors, probably mostly N since the chemical shift of D' is quite close to that observed for pyrolytic BN.

From this very short discussion of the B nuclear magnetic resonance spectra of our $BC_3$ and boron carbonitrides we can conclude that in carbon-rich compounds the boron atoms are likely to form mostly B-B pairs. When the carbon content decreases, so does the proportion of B-B pairs, and larger numbers of B atoms enter B-N bonds.

## REFERENCES

[1] F. Saugnac and A. Marchand, C.R. Acad. Sc. Paris, **310 (II)**, 187 (1990) [2] F. Saugnac, F. Teyssandier, and A. Marchand, J. Chim. Phys. **89**, 1453 (1992) [3] A. Derré, L. Filipozzi, F. Bouyer, and A. Marchand, J. Mater. Sc. **29**,1589 (1994) [4] T. Hagio, M. Nakamizo, and K. Kobayashi, Carbon **27**, 259 (1989) [5] Y.S. Lee and J. Kertesz, J. Soc. Chem. Comm. p 75 (1988) [6] J.P. La Femina, J. Phys. Chem. **94**, 4346 (1990)
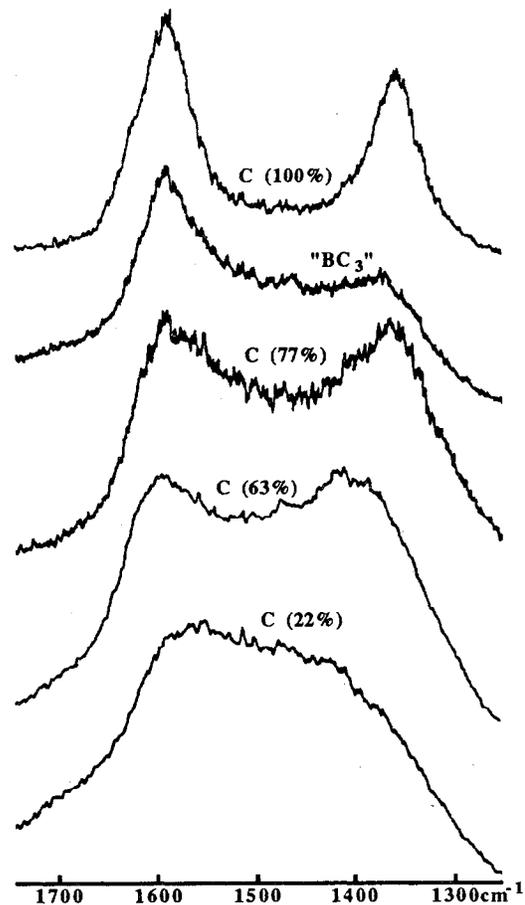
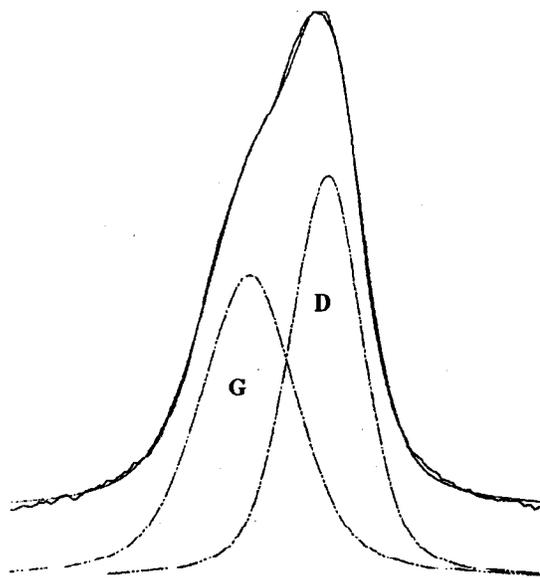Figure 1: Raman spectra of as-deposited films.



Figure 2: computer simulation of the NMR line of "$BC_3$"

321